

HIGH PERFORMANCE POLYMER DEVELOPMENT

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INTRODUCTION

The term high performance as applied to polymers is generally associated with polymers that operate at high temperatures. This is somewhat misleading since there are many polymers that can be classified as high performance materials that perform well in a hostile environment where the temperature is not high. For example, polymeric separation membranes that are resistant to strong chemical action for long periods under stress at ambient temperature or composite matrices on commercial airplanes that must perform over the temperature range of -54 to 93°C for tens of thousands of hours under stress can be classified as high performance polymers. There is no standard definition for high performance polymers because the requirements and environments for different applications vary significantly. In this paper, high performance will be used to describe polymers that perform at temperatures of 177°C or higher. In addition to temperature, other factors obviously influence the performance of polymers such as thermal cycling, stress level, and environmental effects (e.g. moisture, chemical and electrical action).

In regards to high temperature polymers, the worldwide market in 1988 was estimated at 205 million pounds with a value of \$2.3B (ref. 1). This market is expected to double by the end of this decade. New applications for existing materials as well as the introduction of new polymers will contribute to this market increase. High temperature polymers are currently available in many different forms such as adhesives, coatings, composite matrices, fibers, films, foams, membranes and moldings. They are in use or are being considered for use in the following representative applications:

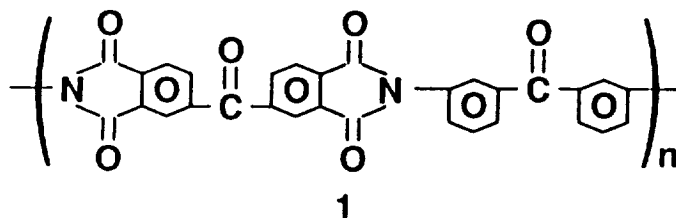
- o Electronic and microelectronic components (circuit boards, moldings, flexible cables, insulators, coatings, wire wraps, etc.).
- o Gaskets, sealants and tubing.
- o Binding systems in brake shoes, abrasive wheels and cutting discs.
- o Structural resins (adhesives, composite matrices, foams) for aircraft, space vehicles, and military items.
- o Jet engine components (fan blades, flaps, ducting, bushings, cowlings, races, etc.).
- o Nuclear reactor components (coolants, insulation, structural parts).
- o Conveyor belts for treating and drying materials.
- o Pipes for chemical processing and energy generators.
- o Fire-resistant materials (protective clothing).
- o Reinforcements (high modulus and high strength fibers and ribbons).
- o Ablators (thermal protection systems).
- o Automotive components (connecting rods, wrist pins, pistons, switches, electrical components).

- o Household items (nonstick interior and decorative exterior surfaces on cookware, irons).
- o Medical devices (prostheses, circuitry in bio-implants, dental instruments).
- o Copier machines (gears and picks).

This paper will discuss some recent developments at NASA Langley in polyimides, poly(arylene ethers) and acetylenic terminated materials. Although our work concentrates on the development of technology for aeronautical applications, primarily structural adhesives and composites, these polymers are potentially useful in other applications.

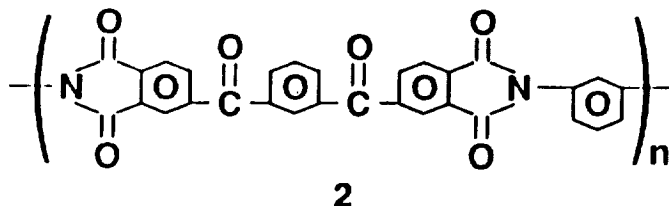
DISCUSSION

Polyimides constitute a major class of high temperature polymers with a market value in 1988 of \$550M. Two principal uses of polyimides are films and moldings. Recent work in our laboratory on new polyimides has been directed towards the development of adhesives, composite matrices, films and moldings. A polyimide designated LARC-TPI (Langley Research Center-Thermoplastic Polyimide) as depicted in structure 1 was initially prepared in our laboratories in the mid 1970s (refs. 2-5). Since the early work on



LARC-TPI, several advances have been made. For example, the molecular weight of the polymer has been controlled and the molecules end-capped to provide a form with a lower melt viscosity (better compression and injection moldability) and better melt stability than high molecular weight unend-capped LARC-TPI. The properties of LARC-TPI are summarized in Table 1. The excellent retention of adhesive properties at 232°C after 37,000 hours at 232°C in air as well as the preliminary laminate properties are particularly noteworthy. LARC-TPI has been licensed and is available as a film, powder, and solution. This material has been successfully developed into a form for injection molding.

An isomeric form of LARC-TPI designated LARC-ITPI and shown in structure 2 has been developed.



The properties of LARC-ITPI are essentially identical to LARC-TPI. The advantage of LARC-ITPI over LARC-TPI is the use of a less toxic diamine (m-phenylenediamine) to make the polymer and the potential of lower cost. LARC-TPI is prepared using 3,3'-diaminobenzophenone, a diamine that exhibited a positive Ames test (mutagenic).

A polyimide similar in chemical structure to LARC-TPI is polyimidesulfone (PIS₀2). The carbonyl group from the diamine portion of the molecule has been substituted with a sulfone group by using 3,3'-diaminodiphenyl sulfone in place of 3,3'-diaminobenzophenone. The sulfone diamine is relatively inexpensive and is non-mutagenic. The mechanical properties of PIS₀2 are similar to those of LARC-TPI.

Another polyimide designated LARC-CPI (Langley Research Center-Crystalline Polyimide) as depicted in structure 3 has also received considerable attention in our laboratories. The properties are summarized in

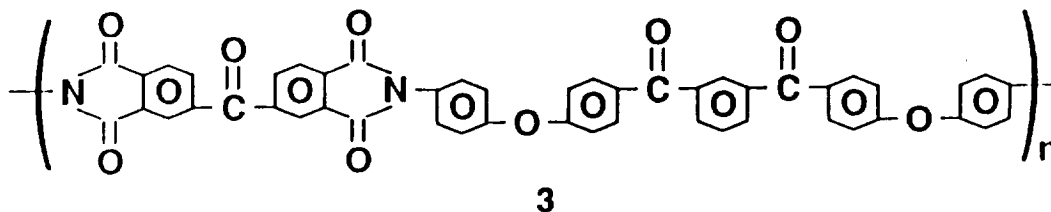
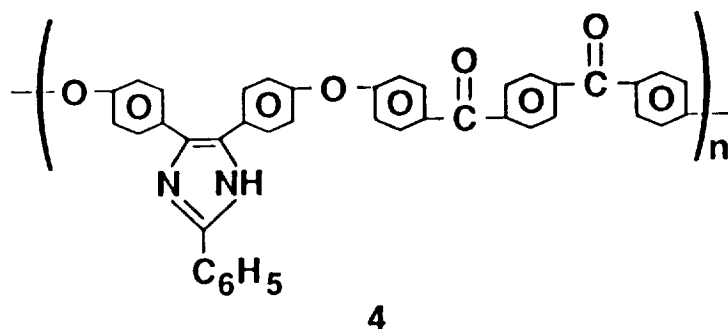


Table 2. The fracture energy as determined on compact tension specimens was extremely high due to the generation of new surface area through cracks and yielding as the crack propagated through the specimen. Films of LARC-CPI have been uniaxially oriented to give 25°C tensile strength and modulus as high as 448.1 MPa (65 Ksi) and 9.65 GPa (1,400 Ksi) respectively. The adhesive properties in Table 1 are impressive. To attain high strength at 232°C, the bonds must be annealed to induce crystallinity in LARC-CPI. Further work has involved molecular weight control and end-capping to provide a form of LARC-CPI that has better compression moldability and faster crystallization rates than high molecular weight LARC-CPI (ref. 13). A controlled molecular weight LARC-CPI has provided adhesive specimens and composites which exhibited high mechanical properties at temperature as high as 232°C.

In the area of poly(arylene ethers), work in our laboratory has concentrated primarily on the incorporation of heterocyclic units within the polymer backbone (refs. 14-16). In general, heterocyclic units in poly(arylene ethers) provides a higher glass transition temperature, higher tensile strength and modulus. Poly(arylene ethers) containing the following heterocyclic units have been prepared. These polymers

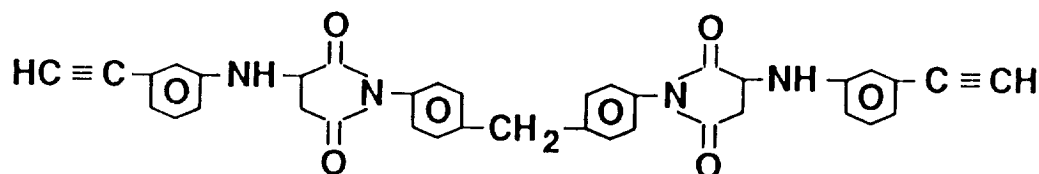
- o Phenyl and substituted phenyl imidazole
- o Phenylquinoxaline
- o Quinoxaline
- o Benzimidazole
- o Benzoxazole
- o 1,3,4-Oxadiazole
- o 1,2,4-Triazole

exhibit a unique combination of properties that classifies them as multipurpose materials. As an example, the properties of a new poly(arylene ether) containing phenylimidazole units as depicted in structure 4 are presented in Table 3.

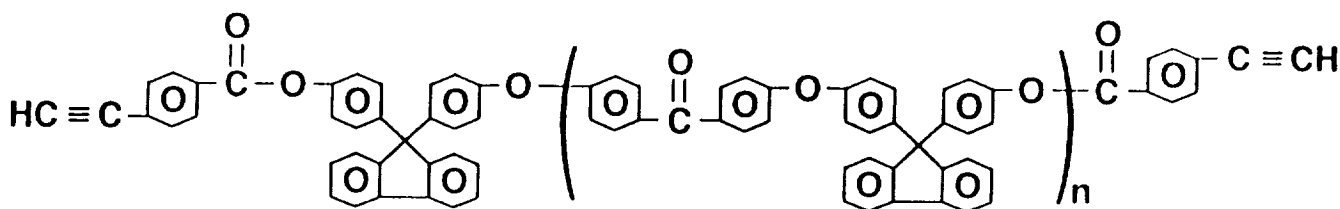


Several poly(arylene ethers) containing heterocyclic units such as the benzoxazole, oxadiazole, quinoxaline and triazole are semi-crystalline. Crystallinity in a polymer generally yields higher modulus and better solvent resistance than an amorphous polymer.

Another approach to the development of high performance/high temperature polymers has involved the use of the ethynyl or acetylenic group. This group has been placed on the ends of molecules, pendent along the polymer chain and within the polymer backbone. Upon heating, it undergoes a complex reaction leading to chain extension, branching and/or crosslinking. In some of our work on ethynyl containing materials, a blend consisting of a low molecular weight ethynyl terminated aspartimide (brittle component) and an ethynyl terminated arylene ether oligomer (tough component) was thermally cured to yield a resin that exhibits attractive neat resin, adhesive and composite properties (refs. 17-18). The chemical composition of the components in the blend are shown in structures 5 and 6. The blend exhibited good compression moldability, allowing for the fabrication of neat resin moldings, adhesive specimens and composites at 250°C under 1.4 MPa (200 psi). The properties of the moldings, adhesive specimens and laminates are given in Table 4.



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CONCLUDING REMARKS

The high performance/high temperature polymers discussed in this paper are representative of the type of work underway at the NASA Langley Research Center. Further improvement in these materials as well as the development of new polymers will provide technology to help meet NASA future needs in high performance/high temperature applications. In addition, because of the unique combination of properties offered by many of these polymers, they should find use in many other applications.

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Table 1 - Properties of LARC-TPI

Glass transition temperature: ~ 250°C
 Density: 1.33 g/cc
 Fracture energy (G_{IC}): ~ 2600 J/m² (15 in lb/in²)

Unoriented Thin Film Properties at 25°C (dried through 1 hr @ 300°C)¹

Tensile Strength, MPa (Ksi)	13.6 (19.7)
Tensile Modulus, GPa (Ksi)	3.72 (540)
Elongation, %	4.8

Ti/Ti Adhesive Properties [RT → 343°C under 1.4 MPa (200 Psi)]

Test Condition	Tensile Shear Strength, MPa (Psi)
25°C	42.6 (6000) ²
232°C	13.8 (2000) ³
232°C after 1000 hr @ 232°C	15.2 (2200) ³
232°C after 10000 hr @ 232°C	24.1 (3500) ³
232°C after 37000 hr @ 232°C	24.1 (3500) ³

Unidirectional AS-4 Laminate Properties⁴, [cured through 1 hour @ 350°C under ~ 2.1 MPa (300 Psi)]

Test Temperature, °C	Flexural St., MPa (Ksi)	Flexural Mod., GPa (Msi)	Short Beam Shear St., MPa (Ksi)
25	1821 (264)	91.0 (13.2)	124 (18.0)
149	1628 (236)	86.9 (12.6)	81 (11.7)
177	1524 (221)	82.8 (12.0)	71 (10.3)

¹Ref. 2²Ref. 3³Ref. 6⁴Ref. 7

Table 2 - Properties of LARC-CPI*

Glass transition temperature: 222°C
 Crystalline melt temperature: 350°C
 Melt viscosity at 395°C at angular frequency of 0.1 rad/sec: 10⁵ Pa·sec (10⁶ poise)
 Equilibrium moisture pickup: < 1%
 Dielectric constant at 1 MHz: 3.1
 Solvent Resistance: Excellent
 Fracture Energy (G_{IC}): 6650 J/m² (38 in lb/in²)

Unoriented Thin Film Tensile Properties (Through 1 hr @ 300°C)

Test Condition	Strength, MPa (Ksi)	Modulus, GPa (Ksi)	Elongation, %
25°C	151.7 (22.0)	4.34 (630)	8.3
25°C after 100 hr soak in 30% aq. NaOH	139.9 (20.3)	4.07 (590)	5.0
177°C	104.8 (15.2)	3.72 (540)	21.1
232°C	35.8 (5.2)	1.69 (245)	76.1
232°C after 100 hr @ 316°C in air	57.9 (8.4)	2.35 (341)	9.6

Ti/Ti Adhesive Properties [RT → 400°C under 6.9 MPa (1000 Psi), hold 15 min @ 400°C]

Test Condition	Tensile Shear Strength, MPa (Psi)
25°C	43.1 (6250)
25°C after 1000 hr @ 232°C	49.1 (7120)
177°C	31.1 (4510)
232°C	4.1 (590)
232°C after 1000 hr @ 232°C	18.9 (2740)
232°C after 100 hr @ 316°C in air	25.3 (3670)

*Ref. 12

Table 3 - Properties of Poly(arylene ether imidazole) 3*

Glass transition temperature: 248°C
Fracture Energy (G_{IC}): 4000 J/m² (22.9 in lb/in²)

Unoriented Thin Film Properties

Test Temp., °C	Tensile St., MPa (Ksi)	Tensile Mod., GPa (Ksi)	Elong., %
25	9.8 (14.2)	2.8 (407)	6.0
177	5.7 (8.2)	2.1 (306)	6.0
200	4.6 (6.6)	1.9 (273)	7.5

Ti/Ti Adhesive Properties [RT → 300°C under 1.4 MPa (200 psi)]

Test Temperature, °C	Tensile Shear Strength, MPa (Psi)
25	33.1 (4810)
93	26.2 (3800)
177	25.5 (3700)
200	21.0 (3050)

*Ref. 15

Table 4 - Properties of Resin from a Blend of Ethynyl Terminated Materials*

Glass transition temperature: 245°C
Fracture Energy (G_{IC}): 675 J/m² (3.8 in lb/in²)
Tensile St.: 93.1 MPa (13.5 Ksi)
Tensile Mod.: 3.6 GPa (525 Ksi)
Elong. (break): 2.6%
Coef. Therm. Expansion: 36.8 ppm/°C

Ti/Ti Adhesive Properties [RT → 250°C under 1.4 MPa (200 psi), hold 0.5 hr]

Test Condition	Tensile Shear St., MPa (Psi)
25°C	22.8 (3300)
25°C after 650 hr @ 200°C, air	17.9 (2600)
150°C	17.2 (2500)
150°C after 650 hr @ 200°C, air	20.5 (2975)
177°C	8.3 (1200)
177°C after 650 hr @ 200°C, air	18.6 (2700)

Unidirectional AS-4 Laminate Properties (cured 1 hr @ 250°C under 1.4 MPa)

Test Temp., °C	Flexural St., MPa (Ksi) [Mod., GPa (Msi)]	Tensile St., MPa (Ksi) [Mod., GPa (Msi)]
25°C	1517 (220) [104 (15.1)]	1917 (278) [121 (17.6)]
150	1462 (212) [100 (14.5)]	1737 (252) [139 (20.2)]
177	1359 (197) [97.2 (14.1)]	—

*Ref. 17